Making Use of Vegetable Residues

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The job of finding out how to utilize millions of tons of vegetable wastes, which have many of the same food elements as the edible parts, but which mostly serve no good purpose, was turned over to us in 1941.

We began by making a survey at farms and processing plants in the Middle Atlantic States to determine what quantities of wastes are available and when. Starting in early spring in the Philadelphia area, spinach waste is found at fresh-market packing houses and at plants processing canned and frozen products. This waste consists of trimmings, inferior leaves, and field wastes.

Pea vines, the next product available, are most plentiful in June and early July. Beet and carrot tops and broccoli leaf waste are found in the field and at packing houses in summer and fall. Lima bean vines are another big waste in late summer and early fall. Celery tops and trimmings are available in late fall, and again in winter from Florida. Turnip and rutabaga tops and kale can be obtained in fair volume in late fall and early winter. Many other vegetable tissues were available in quantities large enough to warrant further study.

Our survey brought out an all-important fact: Something had to be done with the wastes within a very short time after they were harvested if a desirable end product was to be obtained. There are a number of ways to preserve vegetable tissues and prevent their complete breakdown and spoilage. Perhaps the best known are ensiling, as practiced by farmers the world over for preservation of fresh corn and other fodder; freezing, as used in the vegetable-processing industry; and dehydration. Although ensiling and freezing have not been completely ruled out as practical methods of preservation under certain conditions, dehydration was considered the best bet for preservation of most of the materials under the greatest variety of conditions. Reducing the moisture content of a vegetable tissue to approximately 10 percent will give a stable product, which lends itself readily to further laboratory experimentation and commercial application.

Much work has been done on the composition of the edible portions of vegetables, but little on that of the waste portions. Therefore the logical starting point for our research program was a study of certain of the more valuable ingredients. For the laboratory study we obtained some 80 different dried vegetable tissues by separating them by hand into leaves, petioles, stems, and roots. We then dried them on trays in a stream of heated air.

We analyzed the dried ground tissues for crude protein, crude fiber, ether extractables or crude fat, and the two vitamins, carotene, or provitamin A, and riboflavin, or vitamin B_2. Typical analyses of a number of the products studied, which are presented in the first table, show that leaves are highest in protein, fat, and the vitamins and lowest in crude fiber. Stems are low in protein, fat, and vitamins, and usually higher in fiber.

Because the analyses showed a higher concentration of protein and vitamins in the leaves, it seemed desirable to try

1. Composition of typical dried vegetable tissues

Vegetable tissue fraction	Moisture	Proportion of whole top		Chemical analyses (moisture-free basis)				
		Fresh basis	Dry basis	Protein	Crude fiber	Ether extract	Carotene	Riboflavin
							Parts per million	Parts per million
Beet:	Percent	Percent	Percent	Percent	Percent	Percent		
Leaf	90.4	52.6	54.2	27.3	6.0	6.2	568	21.5
Stem	91.0	47.4	45.0	13.6	14.7	1.7	48	7.4
Broccoli:								
Leaf	81.5	36.4	53.7	35.9	7.6	8.5	803	25.6
Petiole and stem	91.0	63.6	46.3	19.0	16.5	3.3	81	8.5
Cabbage, leaf	.....	.....	.....	22.4	8.2	4.7	295	9.9
Carrot:								
Leaf	79.0	51.2	65.1	27.9	10.1	5.6	295	15.7
Stem	88.1	48.8	34.9	11.1	19.3	5.4	41	8.1
Cauliflower:								
Leaf	.....	.....	.....	26.6	9.5	4.1	185	23.2
Petiole	.....	.....	.....	17.1	17.3	.....	28	9.2
Celery:								
Leaf	87.0	.....	.....	27.2	3.5	6.9	352	18.4
Stalk	94.0	.....	.....	12.6	14.3	3.1	11	5.7
Collard:								
Leaf	.....	.....	.....	27.3	6.8	5.3	251	15.8
Petiole	.....	.....	.....	14.8	9.8	.....	28	.....
Corn, sweet, leaf	.....	.....	.....	17.1	26.6	5.5	578	5.5
Kale:								
Leaf	77.3	57.5	63.3	29.4	7.6	5.8	340	21.0
Petiole and stem	82.3	42.5	36.7	16.2	10.0	4.2	21	8
Lima:								
Bean	61.6	20.8	28.1	23.9	6.0	3.7	3	2.4
Leaf	67.7	15.8	18.0	19.4	10.5	6.4	465	12.4
Pod	77.1	25.8	20.9	10.0	37.8	3.0	14	3.7
Stem	74.3	36.9	33.5	9.2	40.1	2.2	36	3.9
Parsnip:								
Leaf	.....	.....	.....	22.9	8.0	5.0	232	11.9
Stem	.....	.....	.....	6.0	17.2	.....	4	4.3
Pea:								
Leaf	65.7	12.3	14.1	21.7	14.4	5.8	346	26.2
Pea	80.1	22.4	19.9	28.8	9.2	1.7	4	7.8
Pod	84.0	35.5	25.2	14.1	18.4	1.2	23	7.8
Stem	67.4	29.9	41.0	11.0	39.2	2.3	47	9.6
Rutabaga:								
Leaf	82.2	36.1	51.4	31.5	6.3	6.5	257	20.9
Stem	90.5	63.6	48.4	18.5	14.9	.....	13	8.5
Turnip:								
Leaf	87.3	46.8	61.9	30.9	7.5	4.4	473	20.3
Stem	93.1	53.2	38.2	18.0	10.3	.....	54	11.6
Spinach:								
Leaf	90.4	45.1	54.7	32.0	6.8	4.1	314	14.6
Stem	93.5	55.0	45.3	22.5	9.3	.....	120	8.5

to work out a method for the best possible separation of the leaves and stems.

This we did by means of a new method, based on the principle of fractional drying. We found that when fresh material was dried in a high-velocity stream of air, at a temperature of approximately 250° F., the thin leaf blades dried more rapidly than the thicker petiole and stem parts of the waste. The dry leaf blade was brittle, and when it was subjected to a breaking and screening action it could easily be separated from the partly wet and tougher stemmy material.

A pilot-plant unit was designed that successfully accomplished the separation of the leafy portions of a number of vegetable wastes. The method was not so successful with pea vines as it was with the wastes having larger leaf surfaces, such as broccoli, kale, and beet and turnip tops. Pea vines could be dried, however, by chopping in a fodder cutter, followed by total drying and hammer milling, with later separation of a leafy fraction by screening. This is the method commonly used in the alfalfa industry for preparing alfalfa leaf and stem meals.

The average yield and composition of leaf meals from various vegetable wastes are shown in the second table.

The yield by the fractional-drying method is much lower than the yield by the total-drying procedure, and the cost of a pound of finished product is higher. The method was designed to produce a leaf meal of highest possible quality, rich in protein and vitamins and low in crude fiber, however, and that has been accomplished. In many cases a greater total yield of a lower-quality product could be obtained by chopping and drying the partly dried stemmy residue. The advisability of using this stemmy fraction would depend upon the economic value of the dried product.

Once the methods for preparing the vegetable leaf meals on a pilot-plant scale had been worked out, we had enough material for studies on their possible value. They appeared to be promising as a supplement for broiler feeds, because diets high in proteins and vitamins and low in fiber are essential to good growth. At the Delaware Agricultural Experiment Station, we tested a variety of leaf meals under many different conditions to show that they make excellent feed supplements. As can be seen in the third table, preliminary investigations established the fact that at a level of 8 percent most of the meals were better than alfalfa as a green supplement and were not toxic to broiler chicks. The rate of growth, feed consumption, and palatability were satisfactory. Pea vines were less valuable as a supplement than the richer leaf meals, but when they were mixed with lima leaf meal they were entirely satisfactory.

The use of some of the meals of higher carotene content at a level of 8 percent of the diet was wasteful of the carotene, and feeding trials showed that much lower levels of the meals could be used to produce good growth. As little as 1 percent of broccoli leaf meal promotes better growth than 5 percent alfalfa leaf meal, as shown in the fourth table.

In other trials, we found that as much as 30 percent of broccoli leaf meal could be added to a broiler diet with no harmful effects. In one trial the chicks did not gain quite so much weight as those that got less leaf meal, but in a second trial no differences were found except for the color and taste. The meat of chicks that had 30 percent meal was dark, like duck meat, at 12 weeks. Some tasters found no resemblance to a cabbagelike taste or odor; some, but not all, liked the richer taste. The shanks and beaks were a deep orange, much too deep in color to make the birds acceptable for marketing. Anyway, the use of 30 percent leaf meal in a diet would be impractical because of cost. Lower levels, from 1.5 percent up, would give more desirable birds. It is apparent, however, that broccoli leaf meal contains no growth-inhibiting factor.

When we found that the carotene in

2. Average yield and composition of leaf meals from vegetable wastes

Vegetable waste	Moisture	Leaf meal: Yield [1]	Leaf meal: Composition (bone-dry basis): Protein	Crude fiber	Ether extract	Carotene	Riboflavin	Yield of wet residue
	Percent	Percent	Percent	Percent	Percent	Parts per million	Parts per million	Percent
Beet tops	92.0	5.6	29.6	6.2	7.6	460	18.4	5.5
Broccoli	88.5	6.6	35.7	6.1	9.5	460	24.7	19.4
Carrot tops	80.7	9.6	18.0	8.5	5.1	158	10.1	32.0
Lima bean leaves	73.8	17.8	21.2	6.9	6.0	297	14.0	8.1
Pea vines	81.5	9.7	14.6	18.8	4.1	85	16.8	[2] 10.7
Rhubarb	88.6	10.7	27.4	6.8	.....	285	7.0	2.4

[1] On basis of fresh material.

[2] Dry residue. Pea vines are totally dried before separation.

3. Results of feeding alfalfa and vegetable leaf meals to chicks

Diet	Analyses of diet: Protein	Crude fiber	Riboflavin	Carotene as vitamin A	Feeding results: Palatability index	Mortality	Average weight	Feed efficiency	Pigmentation index
Basal plus 8 percent of—	Percent	Percent	Parts per million	I. U. per pound		Percent	Pounds	Pounds	
Alfalfa meal	20.8	6.5	1,410	4,500	.....	11	2.55	4.6	48
Pea vine meal	20.0	5.0	1,568	2,200	62	15	2.10	5.1	48
Lima bean vine meal	19.8	4.4	1,290	9,000	78	7	2.51	4.6	59
Turnip leaf meal	20.4	4.5	1,558	21,000	87	11	2.59	4.4	66
Broccoli leaf meal	21.6	4.3	1,976	26,400	96	9	2.73	4.3	95
Carrot leaf meal	19.4	5.2	1,430	5,900	93	6	2.65	4.5	53
Control	20.2	3.8	1,290	1,100	.....	60	1.94	4.7	6

4. Results of feeding low levels of alfalfa and vegetable leaf meals to chicks

Diet	Analysis of diet: Protein	Crude fiber	Ether extract	Riboflavin	Carotene as vitamin A	Feeding results: Mortality	Average weight	Feed efficiency
Basal plus—	Percent	Percent	Percent	Parts per million	I. U. per pound	Percent	Pounds	Pounds
5 percent alfalfa meal	21.1	5.65	4.42	1,122	4,244	6.6	2.70	4.31
1 percent broccoli leaf meal	20.8	5.47	4.26	919	3,790	7.0	2.84	4.24
1 percent broccoli leaf meal plus crystalline riboflavin	20.5	5.26	4.45	2,119	4,167	5.2	3.17	3.82
High-quality commercial broiler mash	24.3	6.57	6.05	1,634	5,911	9.6	3.07	3.84

these leaf meals was an excellent source of vitamin A for poultry, we undertook a test of its activity against vitamin A from fish-liver oil in order to determine its relative economic value. In three feed trials on broiler chicks, standardized amounts of carotene in broccoli leaf meal and in a leaf-meal extract were compared with an equivalent amount of vitamin A ester from fish-liver oil. As shown in the fifth table, growth was better in all groups at 1,500 and 3,000 International Units a pound than at 500 International Units, but even at the lowest level, where a slight difference in efficiency of utilization would be most likely to show, the carotene-fed birds were a little heavier than the chicks fed vitamin A.

In later trials on mature pullets fed exactly equivalent amounts of extracted carotene in oil and vitamin A ester from fish-liver oil, the records of egg laying, fertility, and hatchability showed no significant differences between the groups receiving the two types of vitamin A.

It is apparent that vegetable-leaf carotene, either in the form of the leaf meal or as a concentrate in oil, is just as well utilized, unit for unit, as vitamin A from fish oil by growing chicks and mature poultry.

Although poultry feed offers the best outlet for concentrated feeds like the leaf meals, it is probable that the whole dried waste and dried residues from the preparation of leaf meal might find a use in livestock feeding. A preliminary trial disclosed that whole dried pea vines made a satisfactory feed for sheep. We plan further trials with other livestock.

THE OIL-SOLUBLE FRACTIONS, or lipids, have formed an interesting chapter in the study of the nature of leaf meals. From 3 percent to 10 percent of the meals are soluble in fat solvents, such as petroleum ether and acetone. Fractionation of the ingredients obtained in both analytical and large-scale experiments has led to the separation of many interesting substances. Besides carotene and tocopherols (vitamin E), the leaf meals are rich in sterols, chlorophyll, and xanthophyll.

The leaf sterols may be valuable precursors for the manufacture of sex hormones and the antiarthritic compounds. Chlorophyll, the green coloring matter of plants, has found use as a therapeutic agent in several commercial products and as a deodorant. Xanthophyll is a deep-orange pigment responsible for the yellow color of chick beaks and shanks when a "green" feed is incorporated in the diet. It is also used as a food color.

We can extract and purify the lipids in a number of ways. The method depends on which constituent is desired in greatest purity. Many organic solvents have been used. Among them are petroleum ethers having boiling points 35° to 59°, 63° to 70°, and 88° to 98° C., respectively, and acetone, chloroform, trichloroethylene, and carbon tetrachloride. In general, acetone has been used to obtain chlorophyll; petroleum ether, whose boiling point is 63° to 70° C., has been used for the rest. Analytical procedures for the determination of carotene, xanthophyll, tocopherols, sterols, and chlorophyll have been worked out.

The object of most of the research on the lipids has been to devise procedures that can be used to obtain the maximum number of constituents, because the value of the leaf meal would be proportional to the number of products that could be prepared from it.

We can get the valuable carotene, xanthophyll, tocopherols, and sterols by extracting with hexane, and precipitating out the phospholipids with cold acetone, followed by evaporation of the hexane filtrate in the presence of a vegetable oil. This vegetable oil can then be fractionated by molecular distillation to give concentrates of carotene, tocopherol, and sterol, as outlined in the sixth table.

The carotene concentrate is a deep-red oil containing 15,000 to 30,000 International Units per gram; it is odor-

5. Relative efficiency of vegetable leaf carotene and fish-liver vitamin A esters in broiler feeding

Diet:	Vitamin A	Average weight at 12 weeks	Feed efficiency at 12 weeks	Mortality
	I. U. per pound	*Pounds*	*Percent*	*Percent*
Basal plus—				
Broccoli and lima bean leaf meal	500	2.45	3.72	23.0
	1,500	2.80	3.48	6.5
	3,000	2.92	3.58	6.5
Carotene concentrate	500	2.26	3.80	13.0
	1,500	3.03	3.48	13.0
	3,000	2.81	3.66	10.0
Vitamin A esters	500	2.16	3.85	13.0
	1,500	2.72	3.70	3.3
	3,000	2.95	3.47	10.0

6. Results of molecular distillation of vegetable leaf lipids

Fraction	Appearance	Weight	Carotene		Tocopherol		Sterol	
		Grams	*Percent*	*Grams*	*Percent*	*Grams*	*Percent*	*Grams*
Original oil	Green oil	657.0	0.55	3.40	0.57	3.70	1.45	9.50
Distillate at—								
120° C.	Viscous yellow oil	3.6	0	0	3.1	.11	6.70	.24
140° C.	Orange solid	9.2	0	0	9.3	.86	26.90	2.48
160° C.	....do	9.7	0	0	12.5	1.22	30.20	2.92
180° C.	....do	11.3	(1)	(1)	8.0	.90	20.00	2.25
200–220° C.	Red oil	100.0	1.25	1.25	.42	.42	1.12	1.12
Residue	Green oil	500.0	.18	.90	(1)	(1)	(1)	(1)

[1] Trace.

7. Amino acid content of vegetable leaf meals

[Percentage of amino acid calculated to basis of crude protein (N x 6.25)]

Leaf meal	Protein	Histidine	Arginine	Lysine	Leucine	Isoleucine	Valine	Methionine	Threonine	Phenylalanine	Tryptophane
	Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Pecent*	*Percent*	*Percent*
Beet	24.3	1.3	4.1	5.4	6.4	4.2	5.1	1.7	3.8	5.8	1.2
Broccoli	41.0	1.5	4.8	4.5	6.4	3.2	4.5	1.8	3.3	6.0	1.4
Carrot	19.6	1.2	4.3	4.5	7.1	4.5	5.5	1.7	4.4	6.5	1.4
Celery	23.2	1.5	4.0	2.4	6.8	3.9	4.8	2.2	3.4	4.5	1.3
Corn	19.4	1.3	3.9	3.2	6.9	3.6	4.8	2.8	3.3	5.4	1.3
Kale	24.7	1.6	5.1	3.1	6.5	3.4	4.6	.9	3.5	4.4	1.1
Lima bean	16.9	1.3	4.2	3.6	6.6	3.6	5.0	1.2	4.0	7.0	1.4
Pea vine	23.6	1.6	4.6	4.9	7.8	4.4	5.7	1.0	4.4	6.0	1.5
Rhubarb	26.1	1.9	4.7	5.4	8.4	4.0	5.3	1.0	4.0	6.1	1.6
Spinach	25.7	1.3	4.4	4.7	6.8	3.6	5.0	2.3	3.9	4.7	1.1
Turnip	23.9	1.4	4.5	3.0	6.8	3.9	4.8	2.2	4.0	5.3	1.3

less and bland tasting. The tocopherol concentrate contains 10 to 20 percent tocopherol. The sterol concentrate has 20 to 30 percent sterol. Phytol, a medicinal alcohol, can be obtained in pure form from saponified extracts.

The method is suitable for commercial application because industrial-size molecular stills are in present-day use and their efficiency in separating various oil components is even greater than that of the laboratory stills.

Crude chlorophyll can be obtained from the hexane-extracted leaf meal by extraction with acetone. It can be purified by adsorption on bauxite, elution (washing) with methanol, and concentration of the eluate, from which either oil or water-soluble chlorophyll can be made.

Water-soluble sodium copper chlorophyllin, which has come into wide use for the control of body and breath odors, can best be prepared from vegetable leaf meals by extraction of magnesium chlorophyll with acetone or ethyl or isopropyl alcohol, followed by alkaline methanol saponification. Nonsaponifiables can be removed with hexane and the resulting sodium magnesium chlorophyllin can be converted to the acid chlorin-e by acidification to pH 5. Fatty acids can be removed with hexane at this stage and the hydrogen of chlorin-e can be replaced with copper by boiling with copper acetate in acetic acid. The stable, water soluble sodium salt of copper chlorophyllin can then be made by careful treatment of the moist acid copper derivative with sodium hydroxide in aqueous ethanol. The resulting dried product has a purity of 85 to 90 percent.

Proteins are major constituents of the vegetable leaf meals. Their efficient utilization is necessary if the vegetable wastes are to be economically salvaged. A relatively large amount of protein occurs in the leaf meals and a smaller amount in the stem fractions. When the leaf meals are fed as a source of vitamin A and other vitamin factors, the protein forms a small but definite addition to the protein value of the feed. If markets develop for the lipid constituents of the meals, the plant residue that remains after extraction is a rich source of protein for feed or possible industrial use.

As a feed, the value of the protein depends on its amino acids, because at least 10 of the amino acids are basic elements for building all animal body proteins. Within recent years methods have been developed for the fairly accurate determination of the essential amino acids in crude protein materials such as feeds and vegetable and animal products. The methods are based upon the requirements of certain nonpathogenic bacteria for the various amino acids. By devising synthetic media that contain all but one of the essential amino acids, it is possible to determine quantitatively the amount of any one of 10 acids in an unknown protein solution by comparison with known standards.

The percentages of the 10 essential amino acids found in various leaf meals are listed in the seventh table.

Some degree of purification of the proteins was considered advisable because certain substances which may be present in the crude product are known to interfere with the analyses of the amino acids. Two entirely different methods for separation of nonprotein material were used. Roughly they accomplish the same end, the removal of the large carbohydrate fraction of the vegetable leaf, along with some of the water-soluble sugars and nitrogenous compounds.

Because the solubility of proteins can be greatly altered by drying, we prepared the protein concentrates from fresh or frozen materials. In the first method, the macerated vegetable tissue was fermented with a bacterium known as *Clostridium roseum*. Under the right conditions of temperature and in the absence of oxygen, that organism digests the cell walls of vegetable tissues and leaves the center of the cell relatively intact. This center, known as the protoplast, contains most

8. Average amino acid contents of vegetable leaf meals and vegetable leaf protein concentrates

[Percentage of amino acid calculated to basis of crude protein (N x 6.25)]

	Histidine	*Arginine*	*Lysine*	*Leucine*	*Isoleucine*	*Valine*	*Methionine*	*Threonine*	*Phenylalanine*	*Tryptophane*
	Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
Leaf meals (7).....	1.5	4.4	4.7	7.1	3.9	5.2	1.5	3.9	6.0	1.4
Leaf protoplasts (5)....	1.9	5.9	5.2	9.1	5.3	6.2	1.6	5.0	7.7	2.0
Formic-acid-extracted protein residues (8)...	1.7	5.4	4.7	8.0	4.6	5.6	1.1	4.1	6.9	.55
Formic-acid-extracted protein hydrolyzates(7)	2.0	5.7	5.5	9.0	5.0	6.3	2.1	4.7	6.8	.....
Comparison:										
Purified casein.....	3.1	4.0	7.7	9.9	6.0	7.3	2.8	4.3	6.1	1.2
Purified ovalbumin...	2.2	6.2	6.4	9.1	6.9	7.8	4.4	3.9	8.1	1.2

of the protein and a good deal of lipid material. The solvent extraction of the lipids gives a fairly good concentration of the proteins.

The second method depends on the solubility of proteins in warm formic acid. The vegetable-leaf tissue was frozen to break down the cells, the lipids were extracted with acetone, and the proteins and some carbohydrates were extracted with 90 percent formic acid at 80° C. Most of the carbohydrate could then be precipitated from the final extract with alcohol. The carbohydrate-free protein solution was vacuum-dried, or the amino acids were released by acid hydrolysis for direct determination by the microbiological procedure.

The two products are referred to in the table above as formic-acid-extracted protein residues and formic-acid-extracted protein hydrolyzates.

Instead of presenting the data for each type of leaf, I give the average value in the table for comparison with the average values of the amino acids in the leaf meals. This is justified because of the great similarity of the amino acid contents of the different leaf meals and of the two types of preparations made from the corresponding fresh leaves.

The table shows that the majority of the values found for the amino acids are a little lower in the leaf meals than in the corresponding protoplasts and formic-acid-dried residues and hydrolyzates. In the case of methionine, the value for the leaf meals is from one-half to one-third that in the other preparations. Recovery studies have indicated that methionine is destroyed when carbohydrates in some form are present during acid hydrolysis. The removal of the carbohydrates by fermentation or precipitation allows much greater recovery of the acid. The lower values for the other amino acids in the leaf meals are due probably to the same type of destruction.

If we accept the values found in the protoplasts or formic acid preparations as more nearly correct, it is apparent that those proteins have a nutritionally well-balanced mixture of the 10 essential amino acids and should be entirely suitable as a source of protein.

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